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On the use of polar solvents like acetonitrile and diethyl ether for estimating excited state dipole moments from solvatochromic frequency shifts in electronic spectra

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Abstract: The use of polar solvents like acetonitrile and diethyl ether for estimating molecular excited state dipole moments from frequency shifts in electronic spectra is not quite suitable due to specific interactions and orientation strain exhibited by such solvents towards polar solutes. The use of 'ratio method' is also severely restricted due to inability of majority of solutes to exhibit measurable fluorescence in different solvents. Therefore, for obtaining consistent results from solvent-induced frequency shifts, it is desirable to restrict the spectral measurements in alkane solvents only.

Keywords: Solvent effects, excited states, dipole moment, electronic spectra.

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1. Introduction

According to the well-known theory of solvent effect on electronic spectra (McRae 1957); the solvent-induced frequency shift of an electronic absorption band $\Delta\bar{\nu}_a = \bar{\nu}_{solution} - \bar{\nu}_{vapour}$ is given by an expression of the form :

$$\Delta\bar{\nu}_a = [A + (\mu_g^2 - \mu_e^2)/hca_0^3] f(n) - (2\mu_g \cdot \Delta\mu_{eg}) f(D, n) \quad (1)$$

Here A is a measure of the dispersion and dynamic shifts; μ_g and μ_e are the dipole moments of a solute molecule in its ground- and excited states; $\Delta\mu_{eg} = \mu_e - \mu_g$; h the Planck constant, c the speed of light and a_0 the Onsager cavity radius for the solute molecule; $f(n) = (n^2-1)/(2n^2+1)$ and $f(D, n) = [(D-1)/(D+2) - (n^2-1)/(n^2+2)]$ are the functions of refractive index (n) and dielectric constant (D) of a solvent used; and the last term in the original McRae equation viz., $[(6\mu_g^2 \ [\alpha_g - \alpha_e)/hca_0^6](f(D, n)]^2$ (where α_g and α_e are polarisabilities of the solute molecue in the respective states) is omitted because of its smallness ($\sim 10^1$ cm^{-1}) in comparision with all other terms ($\sim 10^4$ cm^{-1}) as suggested by previous workers (Bayliss and McRae 1954, Nicol 1974). Eq. (1) has been extensively used by several workers for studying solute-solvent interactions.

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By considering spectral measurements in two solvents (denoted as 1 and 2 below) with nearly the same refractive indices ($n_1 \approx n_2$) but widely different dielectric constants ($D_1 \gg D_2$); Ito and coworkers (1960) have simplified eq. (1) to the from :

$$(\Delta\bar{\nu}_a)_{1,2} = -(2\mu_g.\Delta\mu_{eg}/hca_0^3)\Delta f(D)_{1,2} \tag{2}$$

where $(\Delta\bar{\nu}_a)_{1,2} = (\bar{\nu}_a)_1 - (\bar{\nu}_a)_2$ is difference between the frequencies of a solute absorption band in the two solvents and $\Delta f(D)_{1,2} = f(D_1) - f(D_2)$ is the corresponding difference between the dielectric constant functions $f(D) = (D-1)/(D+2)$ of the two solvents. A similar expression for frequency shift of fluorescence bands of a solute in two solvents, viz.,

$$(\Delta\bar{\nu}_f)_{1,2} = -(2\mu_e.\Delta\mu_{eg}/hca_0^3)\Delta f(D)_{1,2} \tag{3}$$

has also been proposed (Baba *et al* 1966, Mugiya and Baba 1967). Further, assuming the structures, cavity radii and direction of the dipole moment vectors in the ground- and excited states of a solute molecule to be respectively the same ; it has been deduced that

$$(\Delta\bar{\nu}_f)_{1,2}/(\Delta\bar{\nu}_a)_{1,2} = \mu_e/\mu_g \tag{4}$$

[Baba *al et* (1983), Mugiya and Baba (1967). Suppan *et al* (1980, 1983)]. The pair of solvents, acetonitrile ($n = 1.344$, $D = 37.50$) and diethyl ether ($n = 1.356$, $D = 4.34$) has frequently been used by several workers (e.g. Ito *et al* 1960, Baba *et al* 1966, Mugiya and Baba 1967. Gosavi and Rao 1967, Suppan and Tsiamis 1980, Suppan 1983, etc.) for evaluting μ_e and/or $\Delta\mu_{eg}$ of various solutes by following the above approach. The 'ratio method' (eq. (4)) has been claimed (e.g. Suppan 1983) to be superior for estimating μ_e valus as it does not contain the empirical a_0 paramater. Though the use of other pairs of solvents, e.g., cyclohexane ($n = 1.420$, $D = 2.02$) and chloroform ($n = 1.448$, $D = 4.81$) also has been suggested (Moxon and Slifkin 1972) ; practically all the reported data corresponds to the use of former pair of solvents only.

Actually, the derivation of McRae's equation (eq. (1)) is based on the assumption of only nonspecific interactions among the solute and solvent molecules (McRae 1957), and so the same must also apply to eqs. (2) to (4) which are deduced from the former. A possibility of specific interactions such as hydrogen bonding (HB) and electron donor-acceptor (EDA) complexation by nonhydrocarbon (nonHC) solvents with polar solutes, and consequently the inadeqaucy of eq. (1) to describe the solvent effect in a general solute-solvent system have been recognised by several workers (e.g. Bayliss and McRae 1954, Bakhshiev *et al* 1969, Yokoyama *et al* 1976, Rao *et al* 1976). The validity and reliabity of the results based on eqs. (2)-(4) would therefore depend on how far the assumption of the absence of

specific interaction is satisfied by the systems under consideration. Therefore, with a view to test general applicability of such approach, the μ_es of several substituted benzenes were recalculated by using eq. (2) and compared with the corresponding values based on the measurements in saturated hydrocarbon (HC) solvents using eq. (1).

2. Results and discussion

The required frequencies of various solute molecules in ether and acetonitrile solvents and the a_0 values are the same as in our previous work (Prabhu Mirashi *et al* 1988, 1989). The previous μ_e values deduced from frequencies in HC solvents using eq. (1) together with the present μ_es, are presented in the accompanying table. As already discussed (Prabhu Mirashi *et al* 1988, 1989), the former μ_es are all larger than the respective μ_gs which is consistent with the general theory of polarisation red shift (McRae 1957), and also in agreement with the general observation of increased contribution of π-dipole moment in excited states due to transfer of lone pair electrons from electron donating substituents like OH and NH_2 to the phenyl nucleus (Mataga and Kubota 1970). Also these μ_es exhibit trends that parallel with those of the respective μ_gs. No such regularities are exhibited by the latter μ_es based on eq. (2). Frequently, these latter μ-values are even smaller than the corresponding μ_g-values, which would imply the corresponding transitions to be of the n-π^* type (Mataga and Kubota 1970). However, the absorption bands of present solutes under consideration are known to originate from π-π^* type transitions only, so that the apparent observation of $\mu_e < \mu_g$ just mentioned is not justifiable.

The above-referred irregularities exhibited by the present μ_e-values are attributable to polar nature of the present solvents, viz., ether and acetonitrile (dipole moments 1.17 and 3.10 D respectively) exhibiting considerable orienentation strain (Bayliss and McRae 1954) towards polar solutes due to which, the assumption of $\vec{\mu}_e /\!/ \vec{\mu}_g$ underlying eq. (2) would not be applicable. These solvents are also known to be capable of specific interactions with proton donor solutes. As already illustrared (Prabhu Mirashi *et al* 1988, 1989), reasonable estimates of specific interaction energies (E_s) of nonHC solvents can be obtained from the difference $\Delta\bar{\nu}_s$ between the observed frequency [$\bar{\nu}_{s(obs)}$] and that calculated [$\bar{\nu}_{s(calc)}$] on the assumptions of only nonspecific interactions ; viz.,

$$E_s = \Delta\bar{\nu}_s \text{ cm}^{-1} = 0.011\Delta\bar{\nu}_s \text{ kJ mol}^{-1}, \tag{5}$$

where the conversion factor 0.011 corresponds to the product of the Planck constant (h), speed of light (c) and the Avogadro number (N). The E_s-values of ether and acetonitrile towards any solule (cf. Table 1) are generally considerably

different, indicating that the strength (and possibly also the type) of such specific interactions depends on the particular solute-solvent system. The choice of ether and acetonitrile as the solvents for estimation of μ_e or $\Delta\mu_{eg}$ may not be much unsatisfactory if the solutes do not have any specific interactions with them as in the case of, e.g. ketones in the original work of Ito *et al* (1960) suggesting the

Table 1. Excited state dipole moments and solute-solvent interaction energies of some substituted benzenes.

	Solute	a_0/Å	μ_g/D	$\leftarrow\mu_e/D\rightarrow$		E_s/kJ mol^{-1}	
				HC	ET/AN	ET	AN
1.	$C_6H_5NO_2$	3.13	4.01	7.22	6 60	17	21
2.	$C_6H_5NH_2$	2 91	1.49	3.76	0.34	8	18
3.	C_6H_5OH	2.93	1 55	5 92	1 51	12	24
4.	$C_6H_5OCH_3$	3.24	1.28	4.01	0.42	−3	3
5.	C_6H_5Cl	2 97	1.88	3 91	1 32	11	19
6.	*o*-$ClC_6H_4NO_2$	3.30	4 64	6.44	4.95	−3	5
7.	*m*-$ClC_6H_4NO_2$	3.30	3 84	7.73	5.53	17	27
8.	*p*-$ClC_6H_4NO_2$	3.26	2.83	10.09	5.01	22	38
9	*o*-$HOC_6H_4NO_2$	3.24	3 13	3 25	3.59	1	0
10	*m*-$HOC_6H_4NO_2$	3 24	3.90	7.12	3.60	−5	9
11.	*p*-$HOC_6H_4NO_2$	3 34	1.83	9.51	8.02	6	14
12.	*o*-$H_2NC_6H_4NO_2$	3.29	4.29	6 67	6.15	−2	1
13.	*m*-$H_2NC_6H_4NO_2$	3.24	4.89	7.61	6.11	−3	6
14.	*p*-$H_2NC_6H_4NO_2$	3.21	6.30	10.74	8.80	3	19
15.	*o*-$H_2CC_6H_4NH_2$	3.14	1 60	5 60	2.37	3	10
16.	*m*-$H_2CC_6H_4NH_2$	3.14	1 45	8.32	3 67	9	18
17.	*p*-$H_2CC_6H_4NH_2$	3.15	1.52	9.34	0.02	4	23
18.	*o*-ClC_6H^4OH	3 12	1 34	4.27	0.39	0	7
19.	*m*-ClC_6H_4OH	3.12	2 19	4 32	1.57	1	9
20.	*p* ClC_6H_4OH	3.10	2.27	5 63	1 52	6	20

HC : Hydrocarbons. ET. Diethyl ether. AN : Acetonitrile.

above approach for estimating μ_es or $\Delta\mu_{eg}$s from solvatochromic frequency shifts. In the present work also it is observed that, when the E_s-values of both these solvents with any solute are quite small (e.g. *o*-nitrophenol or *o*-nitroaniline) or closely comparable (e.g. nitrobenzene) ; the μ_es obtained from the two sets of measurements are reasonably close. However, when the E_s-values of any solute with ether and acetonitrile are considerably different, the μ_es deduced from the corresponding frequencies are no longer comparable with those based on the

frequencies in HC solvents. Since the HC solvents do not exhibit any orientation strain due to their nonpolar nature and also have no specific interacions ; the μ_es deduced from the corresponding frequencies using eq. (1) would be more reliable.

The 'ratio method' which is supposed to be free from the empiricism involved in the choice of the a_0 values, (cf. eq. (4)) also suffers from the some limitations due to use of polar solvents. In addition, the extra assumptions underlying this method viz., the structures, and the directions of the dipole moment vectors of a solute molecule in its ground- and excited states to be the same (Baba *et al* 1966), do not appear quite sound in view of considerable orientation and packing strains due to polar nature of ether and acetonitrile. Further, the application of the ratio method is severely restricted due to the need of the frequency shifts in flourescence spectra, since majority of the solutes are not capable of exhibiting measurable fluorescence in different types of solvents. This last point has also been realised by the authors recommending the ratio method (e.g. Suppan 1983) for estimation of μ_es.

3. Summary and Conclusions

It can therefore be concluded that. though the use of eqs. (2)-(4) appears to offer a simple and convenient method for estimation of μ_es ; in practice, it is quite difficult to realise the desired types of solvent pairs satisfying all the requirements ; viz., of having comparable refractive indices but much different dielectric constants and at the same time being nonpolar so as to exhibit no specific interactions as well as orientation and packing strains towards solute molecules of different types. Such interactions must be considerably altering the electron distribution within a solute molecules so that the μ_es furnished by these equations may not correspond to an isolateds solute molecule. Therefore, in order to obtain meaningful and consistent μ_es from solvatochromic frequency shifts, it is necessary to the restrict absorption spectral measurements in saturated HC solvents and to make use of the original expression of McRae (i.e. eq. (1)). The required value of the cavity radius a_0 for a solute molecule should be calculated from its volume based on its bond lengths, bond angles and atomic van der Waals radii (Prabhu Mirashi and coworkers 1986, 1988, 1989).

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